

Thermal decomposition properties of 1,2,4-triazole-3-one and guanidine nitrate mixtures

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Abstract 1,2,4-triazole-3-one (TO) and guanidine nitrate (GN) have the potential to be used as alternative gas-generating agents. To obtain a better understanding of thermal decomposition properties of TO/GN mixtures, sealed cell differential scanning calorimetry, thermogravimetry–differential thermal analysis–infrared spectroscopy (TG–DTA–IR), and thermogravimetry–differential thermal analysis–mass spectrometry (TG–DTA–MS) were carried out. The endothermic peak and onset temperatures of TO/GN mixtures were lower than those of individual TO and GN. TG–DTA–IR and TG–DTA–MS showed that the mass of TO/GN mixtures decreased with heat generation and N₂ evolved as the major gas during thermal decomposition. The interaction between TO and nitric acid from the dissociation of GN is proposed for the thermal decomposition of TO/GN mixtures.

Keywords 1,2,4-Triazole-3-one · Guanidine nitrate · Thermal analysis · Evolved gas · Real-time analysis

Introduction

In recent years, the uses for energetic materials have become quite diverse and include air-bag systems, synthesis technology, and medical technology. Gas-generating agents have received considerable attention due to their

potential applications. These agents require specialized control for effective operation. 3-Nitro-1,2,4-triazole-5-one (NTO) has the equivalent amount of energy release as 1,3,5-trinitroperhydro-1,3,5-triazine or 1,3,5,7-tetranitroperhydro-1,3,5,7-tetrazocine, but with greater thermal stability [1–3]; therefore, NTO is used as a propellant powder for military use. 1,2,4-Triazole-3-one (TO; Fig. 1), which has an identical framework to NTO, is anticipated to exhibit greater stability and higher reactivity. The thermal stability and gases evolved from TO derivatives have been reported [4, 5]; however, the reactivity of TO and mixtures of TO and nitrate salts have yet to be fully understood. TO derivatives are expected to become alternative gas-generating agents with optimized performance. Guanidine nitrate (GN; Fig. 1) is a gas-generating agent used with propellants, of which the thermal decomposition [6] and combustion [7] characteristics have been reported.

To obtain a better understanding of the thermal decomposition properties of TO/GN mixtures, sealed cell differential scanning calorimetry (SC-DSC), thermogravimetry–differential thermal analysis–infrared spectroscopy (TG–DTA–IR), and thermogravimetry–differential thermal analysis–mass spectrometry (TG–DTA–MS) experiments were performed.

Experimental

Materials

TO was obtained and confirmed the structure by employing a previously reported method [4, 8]. Reagent-grade purity GN (>98%, Tokyo Kasei Kogyo Co., Ltd.) was used as-received. Testing mixtures TO/GN (w/w) = 0/10, 1/9, 3/7, 5/5, 7/3, 9/1, and 10/0 were prepared.

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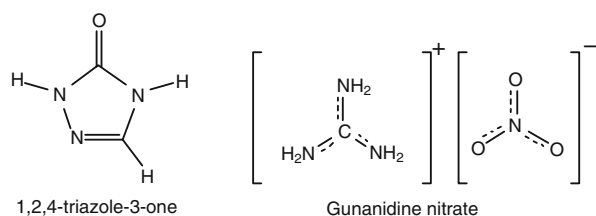


Fig. 1 Molecular structures of TO and GN

Instruments

SC-DSC (Mettler Toledo, HP DSC827e) was conducted with 1-mg samples in stainless-steel sealed cells (Seiko Instruments Inc.) at a heating rate of 10 K min⁻¹ over the measurement range of 25–500 °C.

TG-DTA-IR was used to identify the decomposition gases evolved from the pyrolysis of TO/GN mixtures. The apparatus consisted of two parts: a TG (Shimadzu Co. Ltd., DTG-50) system and an IR spectrometer (Shimadzu Co. Ltd., IRPrestige-21). The gases evolved after pyrolysis of the samples (2 mg) were supplied to a gas cell for IR analysis through a stainless-steel transfer line. TG-IR was carried out using an aluminum pan under an argon gas flow of 20 mL min⁻¹ with the following conditions: heating rate, 10 K min⁻¹; measurement range, room temperature (RT; 25–30 to 400 °C); transfer line and IR gas cell temperature, 200 °C; scanning resolution, 8 cm⁻¹. The spectra were integrated 15 times.

TG-DTA-MS was employed for real-time analysis of the gas evolved from TO pyrolysis. The TG-DTA-MS apparatus consisted of two parts: a TG (Rigaku Co., TG8120) system and a mass spectrometer (Shimadzu Co., GCMS-QP2010). TG-DTA-MS was conducted using an aluminum pan under a helium gas flow of 200 mL min⁻¹ with the following conditions: heating rate, 10 K min⁻¹; measurement range, RT–400 °C; oven temperature, 200 °C. The components of the evolved gases were identified on the basis of IR and MS reference spectra, available in the National Institute of Standards and Technology (NIST) spectral libraries [9].

Results and discussion

Thermal analysis

Figure 2 shows the SC-DSC curves of TO/GN mixtures = 0/10, 1/9, 3/7, 5/5, 7/3, 9/1, and 10/0. Table 1 lists the endothermic peak temperatures, onset temperatures (T_{DSC}), and heats of decomposition (Q_{DSC}) obtained by SC-DSC. Both individual TO and GN samples (TO/GN = 10/0, 0/10) an endothermic peak that corresponded to melting, and an exothermic peak. The endothermic peak

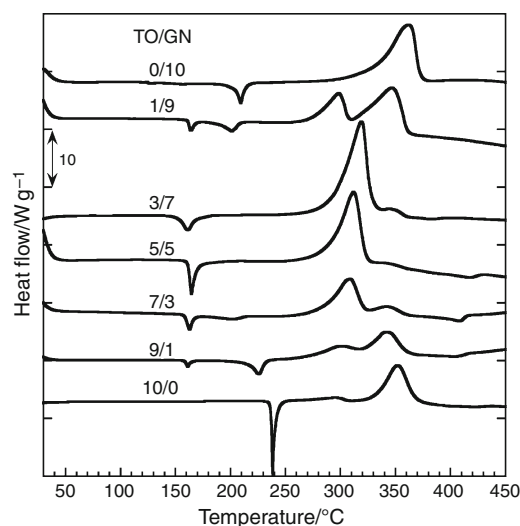


Fig. 2 DSC curves measured for TO/GN mixtures in sealed SUS cells at a heating rate of 10 K min⁻¹

Table 1 Results of thermal analysis of TO/GN mixtures

TO/GN	Endothermic peak/°C	$T_{TG5\%}/^{\circ}\text{C}$	$T_{DTA}/^{\circ}\text{C}$	$T_{DSC}/^{\circ}\text{C}$	$Q_{DSC}/\text{kJ g}^{-1}$
0/10	216	285	–	279	1.8
1/9	167	244	243	248	2.3
3/7	167	221	247	247	2.5
5/5	167	209	251	248	1.9
7/3	167	208	258	244	1.8
9/1	166	206	264	248	1.1
10/0	239	204	–	332	1.0

and T_{DSC} of TO/GN mixtures (TO/GN = 1/9, 3/7, 5/5, 7/3, and 9/1) were lower than those of TO and GN, and two exothermic peaks were observed in the DSC curves. TO/GN = 1/9 clearly showed two exothermic peaks in the DSC curve. The exothermic peak in the range 250–310 °C is considered to be a reaction between TO and GN. And another exothermic peak in the range of 310–360 °C is thought to be decomposition of excess GN. The mixing ratio had little influence on the endothermic peak temperatures and T_{DSC} . TO/GN = 5/5 exhibited a solid-to-liquid phase transition with an endotherm according to the DSC measurement using an open cell. Q_{DSC} for TO/GN = 3/7 was larger than those of the other ratios.

TG-DTA curves for the mixtures of TO/GN = 0/10, 3/7, 5/5, 7/3, 10/0 are shown in Fig. 3. The TG-DTA results are summarized in Table 1 and show the temperatures at 5% mass loss ($T_{TG5\%}$) and the onset temperatures (T_{DTA}). The mass loss of TO began at 197 °C, with two endothermic peaks indicating the melting and vaporization of TO [4]. GN showed mass loss with an endothermic peak followed by another endothermic peak indicating melting.

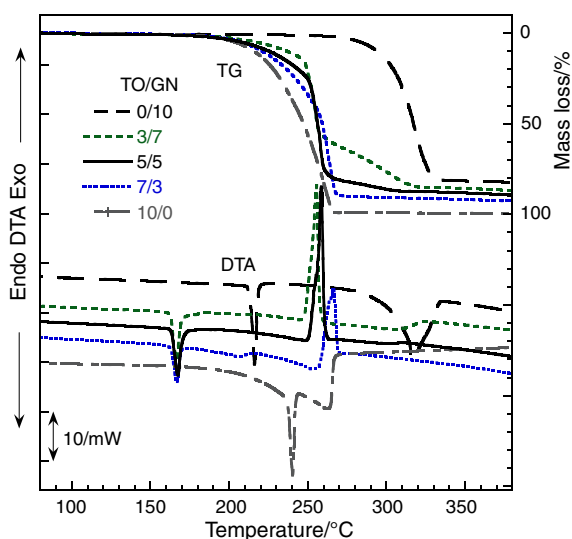


Fig. 3 TG–DTA curves of TO/GN mixtures at a heating rate of 10 K min^{-1}

The TO/GN mixtures showed a sharp mass loss with exothermic peaks in the range of $243\text{--}264 \text{ }^\circ\text{C}$. This mass loss is considered to be a reaction between TO and GN. When the mixing ratio of GN was increased, $T_{\text{TG}5\%}$ and the amount of residue at $400 \text{ }^\circ\text{C}$ increased and T_{DTA} slightly decreased. The maximum heat release rate was the highest when the TO/GN mixture ratio was 5/5. The SC-DSC and TG–DTA results indicate that the mass of the TO/GN mixtures decrease with heat generation in the range of $243\text{--}264 \text{ }^\circ\text{C}$, and TO/GN = 3/7 had the largest Q_{DSC} . The thermal decomposition of TO/GN mixtures accelerates interaction of each component in the mixtures under open conditions, although the thermal behavior of individual TO had no reaction due to vaporization.

Evolved gas

Evolved gas analyses were performed using TG–DTA–IR and TG–DTA–MS. Figure 4 shows an IR spectrum of gases evolved from TO/GN = 3/7 at $400 \text{ }^\circ\text{C}$, and averaged MS spectra of gases evolved from various TO/GN mixtures are shown in Fig. 5. The IR spectral peaks are assigned to νHCN : $3200\text{--}3350 \text{ cm}^{-1}$, νCO_2 : $2300\text{--}2400 \text{ cm}^{-1}$, νHNCO : $2250\text{--}2275 \text{ cm}^{-1}$, $\nu\text{N}_2\text{O}$: 2225 cm^{-1} , and δNH_3 : $920\text{--}970 \text{ cm}^{-1}$. The peaks in the mass spectrum correspond to mass-to-charge (m/z) ratios of 44, 43, 42, 30, 28, 27, 18, 17, and 16. The results indicate that the gases evolved from TO/GN mixtures at $400 \text{ }^\circ\text{C}$ are N_2 , CO_2 , N_2O , H_2O , NH_3 , and HCN . Since the main peak was $m/z = 28$ in the mass spectrum, the evolved gases from TO/GN mixtures have larger amounts of N_2 than other evolved gases. Although the $m/z = 28$ peak was also considered to be a fragment of CO_2 , the $m/z = 28$ peak

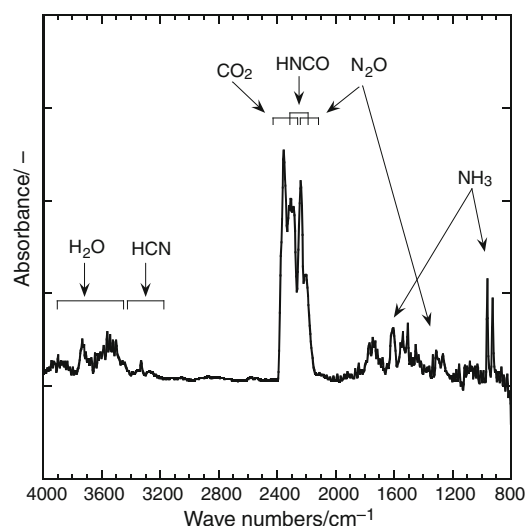


Fig. 4 IR spectrum of gases evolved from TO/GN = 3/7 measured at $400 \text{ }^\circ\text{C}$

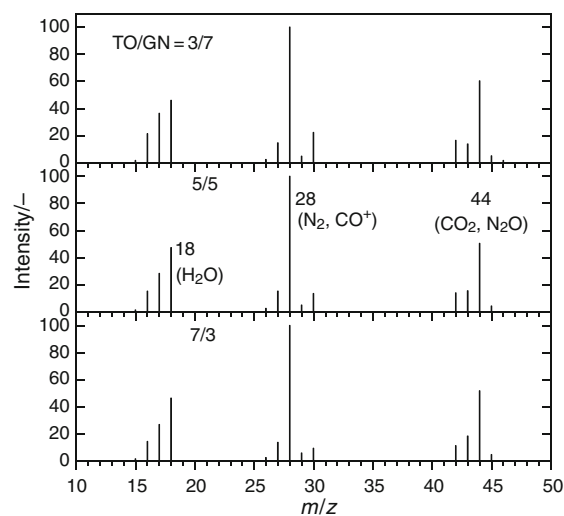


Fig. 5 MS spectra of gases evolved from various TO/GN mixtures using TG–DTA–MS at a heating rate of 10 K min^{-1}

exhibited higher intensity than the $m/z = 44$ peak due to N_2O and CO_2 .

Real-time analysis of the evolved gases was carried out using TG–MS. Figure 6 shows TG curves for TO/GN mixtures in addition to total ion current (TIC) curves. The TIC curves of TO/GN = 3/7 and 5/5 display two peaks. The first peak ($245\text{--}275 \text{ }^\circ\text{C}$) corresponds to the mass loss exotherm, and a second small peak ($275\text{--}320 \text{ }^\circ\text{C}$) was observed with increasing mixing ratio of GN. The small second peaks are considered to be due to the decomposition of products and to excess GN. All of the MS spectra of the first peaks in the TIC curves have a similar pattern, and it is reasonable to speculate that the exothermic decomposition is the result of similar reactions, regardless of the mixing ratios.

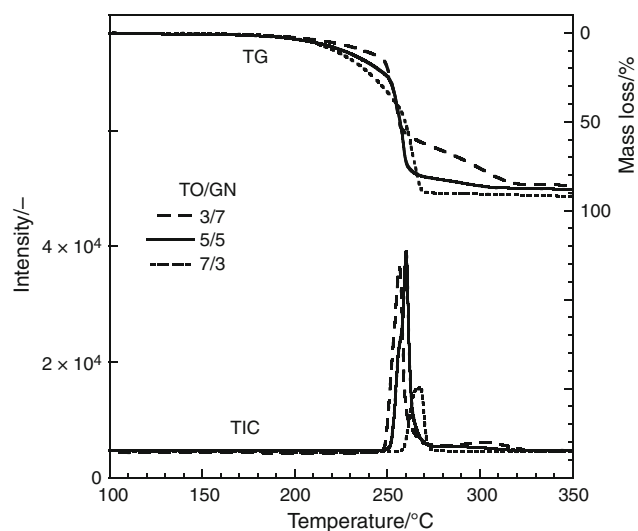


Fig. 6 TG–TIC curves of various TO/GN mixtures measured using TG–DTA–MS at a heating rate of 10 K min^{-1}

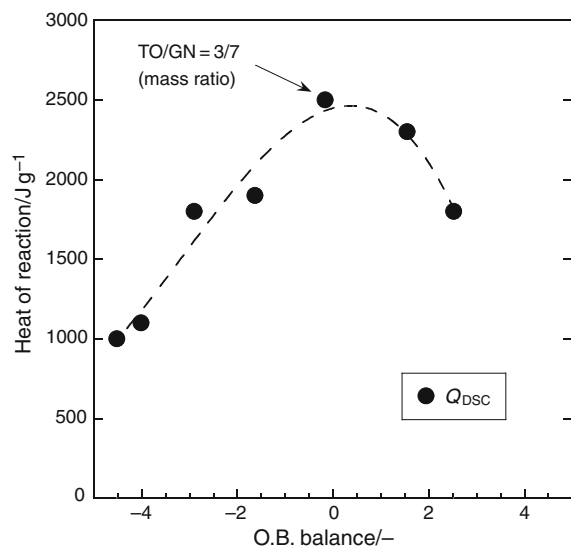


Fig. 7 Heat of reaction versus oxygen balance of TO and nitric acid from GN

Thermal decomposition properties

From the results of the thermal analysis and evolved gas analysis, the thermal decomposition of TO/GN mixtures was considered to be a reaction between TO and nitric acid from the dissociation of GN. TO/GN mixtures decomposed by an exothermic reaction with mass loss and evolved gases that differed from individual TO and GN. TO/GN = 3/7 had the largest Q_{DSC} ; however, the mass ratio in terms of the equal mole ratio was TO/GN = 4.1/5.9. The decomposition process for the dissociation of GN to nitric acid and guanidine with melting has already been proposed

[6]. When TO reacts with nitric acid, the equivalent mole ratio is TO/nitric acid = 1/1.8, of which the corresponding equivalent mass ratio of TO/GN is 2.8/7.2. Figure 7 shows the Q_{DSC} results plotted against the oxygen balance of TO and nitric acid from GN. When the oxygen balance of TO and nitric acid becomes almost zero (TO/GN = 3/7), then Q_{DSC} reaches a maximum, which supports the proposed decomposition process of TO and GN.

Conclusions

Based on the investigations of the thermal decomposition properties of TO/GN mixtures, the following conclusions were drawn.

1. TO/GN mixtures react with exothermic heat and evolution of gases in the range of 243–264 °C.
2. Q_{DSC} for TO/GN = 3/7 was larger than those of other mixing ratios.
3. The gases evolved from TO/GN mixtures at 400 °C were determined to be N_2 , CO_2 , N_2O , H_2O , NH_3 , and HCN.
4. N_2 was the major gas for the thermal decomposition of TO/GN mixtures.
5. The interaction between TO and nitric acid is proposed for the thermal decomposition of TO/GN mixtures.

References

1. Sinditskii VP, Smirnov SP, Egorshv VY. Thermal decomposition of NTO: an explanation of the high activation energy. *Propellants Explos Pyrotech.* 2007;32:277–87.
2. Thangadurai S, Karatha KPS, Sharma DR, Shukla SK. Review of some newly synthesized high energetic materials. *Sci Technol Energ Mater.* 2004;65:215–26.
3. Hara Y, Taniguchi H, Ikeda Y, Takayama S, Nakamura H. The thermal decomposition and hazards evaluation for 3-nitro-1,2,4-triazol-5-one. *Sci Technol Energ Mater.* 1994;55:183–7.
4. Yoshino S, Ihara S, Matsunaga K, Miyake A. Synthesis and thermal behavior of 2,4-diaryl-3H-1,2,4-triazole-3-ones. *Sci Technol Energ Mater.* 2009;70:16–22.
5. Yoshino S, Miyake A. Pyrolysis mechanism of urazole by evolved gas analysis. *J Therm Anal Calorim.* 2009. doi:10.1007/s10973-009-0571-9.
6. Oxley JC, Smith JL, Naik S, Moran J. Decompositions of urea and guanidine nitrate. *J Energ Mater.* 2009;27:17–39.
7. Damse RS. Studies on the decomposition chemistry of triamino-guanidine azide and guanidine nitrate. *J Hazard Mater.* 2009;172:1383–7.
8. Haines DR, Leonard NJ, Wiemer DF. Syntheses and structure assignments of six azolinone ribonucleosides. *J Org Chem Res.* 1982;47:474–82.
9. NIST Chemistry Webbook Standard Reference Database. 2005. p. 69.